ORIGINAL PAPER

Insight into selection of appropriate formulation for colloidal gas aphron (CGA)-based drilling fluids

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Abstract

Application of light-weight drilling fluids is essential to develop depleted hydrocarbon reservoirs. Recently, colloidal gas aphron (CGA)-based fluids have been introduced for such applications due to their ability in controlling fluid losses. In this work, a comprehensive experimental study was performed to choose the best formulation for CGA fluids by implementing static stability tests, rheological behavior measurements, and bubble size analyses of CGAs. Xanthan gum polymer and sodium dodecyl benzene sulfonate (SDBS), an anionic surfactant, and cetyl trimethyl ammonium bromide (CTAB), a cationic surfactant, were utilized to prepare CGAs. For the range of experiments conducted, the performance of CGA fluids prepared with SDBS was improved by increasing the polymer and surfactant concentrations. However, for CTAB, it was improved by an increase in the polymer concentration and a decrease in the surfactant concentration. The formation of white, long hair-like precipitates observed at high levels of CTAB caused CGA fluid to become rapidly unstable. Also, it was observed that the size of CGAs was significantly influenced by the polymer and surfactant concentrations. The most stable bubbles were formed at 6.86 g/L of polymer concentration. The results of this study provide insights into appropriate formulation for CGA-based fluids which could be potentially applicable in drilling operations.

Keywords Colloidal gas aphrons · Dispersion · Stability · Rheology · Bubble size analysis

1 Introduction

Colloidal gas aphron (CGA)-based fluids were successfully used in the petroleum industry to drill through depleted oil and gas reservoirs and low-pressure formations (Brookey 1998; Ivan et al. 2001; Kinchen et al. 2001; MacPhail et al. 2008; Ramirez et al. 2002). This fluid system has been proven to have many advantages such as minimal fluid invasion, eliminating intermediate casing, reducing rig days, and rapid cleanup during production phase. Aphrons were first introduced as unique microbubbles with unusual characteristics (Sebba 1987). Their small size (25 to several hundred microns in diameter) gives them colloidal properties, and hence, they are also known as colloidal gas aphrons. Aphrons are comprised of a spherical core of air and a protective multilayer film. This film, which is the key to maintaining bubble stability, enables the aphrons to function as a stable drilling fluid. Unlike conventional air bubble, which is stabilized by a surfactant monolayer, the outer shell of an aphron is thought to consist of a much more robust surfactant tri-layer (Fig. 1) (Sebba 1987). This tri-layer film is composed of an inner surfactant layer enveloped by a viscous water lamella, which is overlaid with a surfactant bilayer that provides rigidity and low permeability to the whole structure.

Aphrons form a major part of the drilling fluid at atmospheric pressure (usually 10–15 vol%) (Growcock et al. 2006). Concentration of aphrons in drilling fluid is controlled through the surfactant and polymer concentrations. At downhole pressures, aphrons form an insignificant volume, e.g., a mud sample containing 12 vol% nitrogen at atmospheric pressure will contain less than 0.06 vol% nitrogen at 3000 psig (Growcock et al. 2006).

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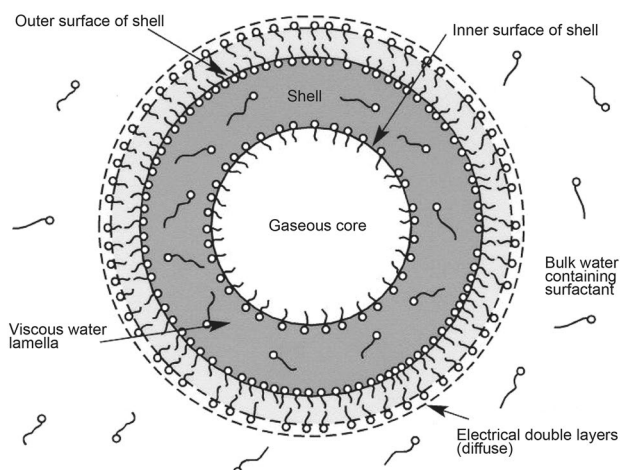
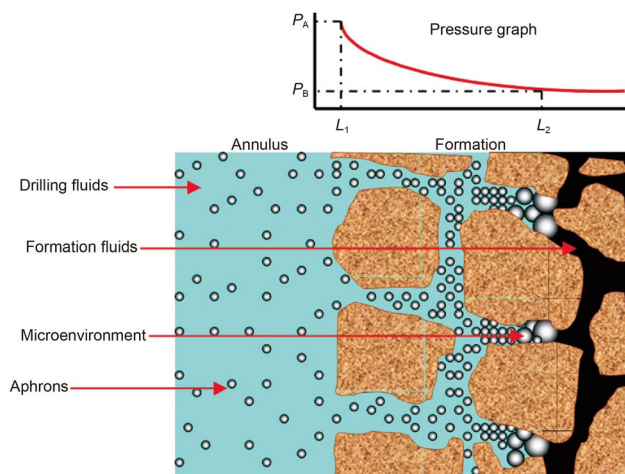**Fig. 1** Structure of a CGA proposed by Sebba (1987)

Fig. 2 Aphrons bridging mechanism (Gaurina-Međimurec and Pašić 2009)

Thus, aphrons have little effect on mud density. When the aphron-based drilling fluid enters a formation with a pressure lower than that of the borehole, the aphrons expand and will concentrate at the fluid front to create a "microenvironment" that separates the borehole from the formation pressures, effectively putting the borehole and formation "at-balance" (Fig. 2), thereby reducing the fluid invasion and controlling the fluid loss into the formation (Gaurina-Međimurec and Pašić 2009).

In formulation of CGA-based fluids, three major elements exist: base fluid (in this study, water), polymer as viscosifier and aphron stabilizer and surfactant as aphronizer. Polymer is an important component of the CGA-based fluid which stabilizes the aphron structure. It viscosifies the water

"lamella" that surrounds the aphron core and strengthens the bubble film so that the aphrons can survive for a long period of time. It is also used to improve mud rheological properties such as shear viscosity and low shear rate viscosity. Surfactant is another essential element of the CGA, which converts the entrained air into highly stabilized aphrons. Surfactant molecules build the multilayer film and create interfacial tension to form a non-bonding network of bubbles capable of sealing openings in high-permeability and fractured formations. The surfactant type (based on the charged group on the surfactant head) affects the stability and also other physicochemical characteristics of the produced CGAs. Therefore, selection of a suitable surfactant plays an important role in the preparation of CGAs with desired rheological and filtration properties.

The stability of CGA-based fluids has been a subject of many studies. The stability of CGA-based fluids is defined as the ability to resist changes in bubble size, liquid content, or degree of dispersion. According to Sebba (1987), if a CGA-based fluid is remained unstirred, it will separate into foam phase and liquid phase. This is due to the density difference between aphrons and the liquid phase. Arabloo and Pordel (2014) conducted static drainage tests and poured 150 mL of the freshly prepared CGA-based fluid into a graduated cylinder. They found that the polymer (XG) concentration has a great effect on the stability of CGA dispersions. Also, the bubble size of CGAs and their size distribution are important parameters to the efficient bridging of pores. To quantify the pore blocking ability of CGA fluids, these parameters should be known. Bjorndalen and Kuru (2008a) used changes in aphron diameter with time to investigate the CGAs stability by using a microscopic imaging technique. In another study, Bjorndalen and Kuru (2008b) found that the size of aphron bubbles generated using anionic surfactants was smaller than those generated using cationic surfactants. Arabloo and Pordel (2014) measured the size and size distribution of CGAs prepared with XG polymer and SDS (sodium dodecyl sulfate) surfactant. They found that the initial aphron bubble size increases with increasing SDS concentration and decreases significantly with the polymer concentration.

In this study, a comprehensive experimental study was conducted to choose the appropriate formulation for CGA-based fluids using static stability tests, rheological behavior measurements, and bubble size analyses of CGAs simultaneously. Xanthan gum (XG) polymer and sodium dodecyl benzene sulfonate (SDBS), an anionic surfactant, and cetyl trimethyl ammonium bromide (CTAB), a cationic surfactant, were chosen to prepare CGA-based fluids.

Effects of surfactant type and polymer and surfactant concentrations on the physicochemical characteristics of CGA-based fluids were studied. The experimental observations and interpretations are presented in detail within a new framework. Also there are some new findings on CTAB-based CGA fluids which are presented here for the first time in this study and were not addressed in previous works.

2 Experimental procedure

2.1 Materials

XG polymer solutions with concentrations of 4.57, 5.71, and 6.86 g/L (in 350 cm^3 of distilled water) were used in this study as viscosifier. Two different types of surfactants were chosen for this study: SDBS, an anionic surfactant, and CTAB, a cationic surfactant, each one at three levels of concentration. Surfactant concentrations were designed in such a way to enable us compare properties of CGA-based fluids with respect to critical micelle concentration (CMC) of each surfactant. Thus, concentrations of 0.34 g/L (below CMC), 0.57 g/L (CMC) and 0.80 g/L (above CMC) were chosen for SDBS surfactant and 0.35 g/L (CMC), 1.43 g/L and 2.14 g/L (above CMC) for CTAB surfactant. CMC values for these two surfactants were adopted from the literature (Mukerjee and Mysels 1971).

2.2 Preparation of the base fluid and the CGA fluid

The base fluid was prepared by mixing XG polymer at the above-mentioned concentrations in 350 mL of distilled water for 20 min at a speed of 8000 rpm in a Hamilton Beach mixer, where it is further aphronized. Optimum conditions for preparation of the CGA fluid were determined as part of another work. For SDBS, the mixing time

of 5 min and the mixing rate of 6000 rpm, and for CTAB, the mixing time of 5 min and the mixing rate of 8000 rpm were found to be optimum conditions for the preparation of CGA fluids. Accordingly, the CGA fluids used in the following were prepared at these optimum conditions. Table 1 shows formulation of CGA-based fluids used in this study.

2.3 Characterization tests

To study the stability of CGA fluids, static drainage experiments were conducted in 250 cm^3 measuring cylinders. Volumes of the drained liquid and the foam phase were recorded with time to measure the stability of CGA-based fluids. Also, the rheological behavior of CGA-based fluids was studied with a Fann viscometer (Model 35). Fann readings were converted to shear stress, shear rate, and viscosity data using appropriate formulas. Finally, the bubble size analysis of CGAs was performed to quantify the stability of CGA bubbles with time. To achieve this, CGA fluid samples were placed on a microscope glass slide and then magnified using an optic microscope to obtain pictures with a charge-coupled device (CCD) camera attached to the microscope. The pictures were analyzed by "ImageJ" software to obtain d_{50} and d_{90} as well as the bubble size distribution of CGAs. The values for d_{50} and d_{90} are defined as the diameters in which 50% and 90% of the bubbles population are less than that specific diameter, respectively. About 300–500 bubbles were counted for each sample to ensure representative size distribution. Bubble size analyses were performed several times to ensure unique behavior of aphrons. For pictures at time $t = 0$, care was taken to ensure that pictures are obtained immediately following the aphron preparation. To measure the diameter and size distribution of bubbles at later times, samples were taken by pipette from bottom of the measuring cylinder where aphrons had not affected by coarsening at top of the measuring cylinder.

Table 1 Formulation of CGA-based fluids prepared with SDBS and CTAB

Sample No.	SDBS concentration, g/L	XG concentration, g/L	Sample No.	CTAB concentration, g/L	XG concentration, g/L
S1	0.34	4.57	S10	0.35	4.57
S2	0.57	4.57	S11	1.43	4.57
S3	0.80	4.57	S12	2.14	4.57
S4	0.34	5.71	S13	0.35	5.71
S5	0.57	5.71	S14	1.43	5.71
S6	0.80	5.71	S15	2.14	5.71
S7	0.34	6.86	S16	0.35	6.86
S8	0.57	6.86	S17	1.43	6.86
S9	0.80	6.86	S18	2.14	6.86

3 Results and discussion

3.1 Stability of CGA fluids

Static stability of CGA fluids was determined by the rate at which the based liquid drained from the foam phase. This drainage occurs because of the density difference between microbubbles and the bulk phase; the bubbles move upward while the base liquid drains downward. The results of static stability tests for fluid samples prepared with SDBS are plotted in Fig. 3. At a constant concentration of polymer, the surfactant concentration did not strongly affect the stability and liquid drainage of the CGA-based fluid, while an increase in the polymer concentration improved the fluid stability considerably. An increase in the polymer concentration raises the base fluid viscosity and hence makes the viscous layer of aphrons more impermeable against the loss of air from the gaseous core to the bulk phase. Consequently, there would be a more stable CGA fluid. Furthermore, by viscosifying the base fluid, water molecules in the viscous layer of lamella are preserved and a more durable film against diffusion of air will be formed.

From Fig. 3, one can conclude that for fluid samples S7, S8 and S9 (samples with highest polymer concentrations), the drainage rate is lower and theses samples are more stable. As noted above, the lower drainage rate for S7, S8 and S9 samples is due to the difficulty of movement of bubbles to top of the measuring cylinder through more viscous CGA fluid samples. One should note that the higher final drained volume of S7, S8 and S9 samples does not mean that these samples had higher drainage rate values and hence were less stable; but it means that these samples had higher base fluid content in 250 mL of dispersion.

Another promising method to quantify the stability test results is to measure the half-life time for each sample, defined as "the time taken for half of the base liquid to drain out from the aphronized fluid" (Sebba 1987). Half-life times obtained from these samples are reported in Table 2. As expected, samples with the highest polymer concentration were more stable and had the longest half-life time. Hence, from the stability test viewpoint, samples prepared with 6.86 g/L XG polymer concentration were preferable than other samples.

Static stability test results for fluid samples prepared with CTAB surfactant are presented in Fig. 4. For most of the samples, phase segregation occurred immediately after the CGA fluid was poured into the measuring cylinder. Microscopic pictures of aphrons prepared by CTAB and XG polymer revealed the formation of white, long hair-like precipitates, possibly due to the chemical reaction between CTAB and XG polymer (Fig. 5b). This phenomenon was also reported by Bjorndalen and Kuru (2008b). It is thought that
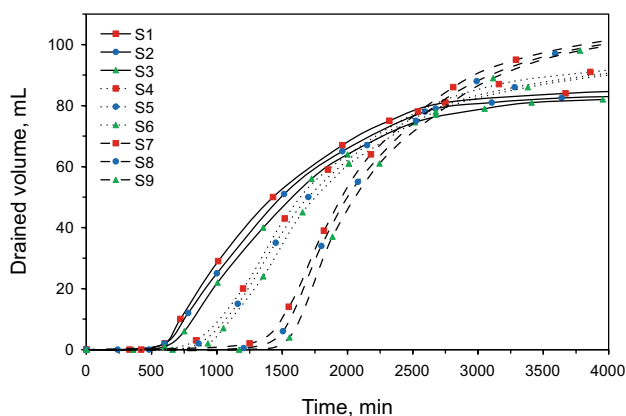

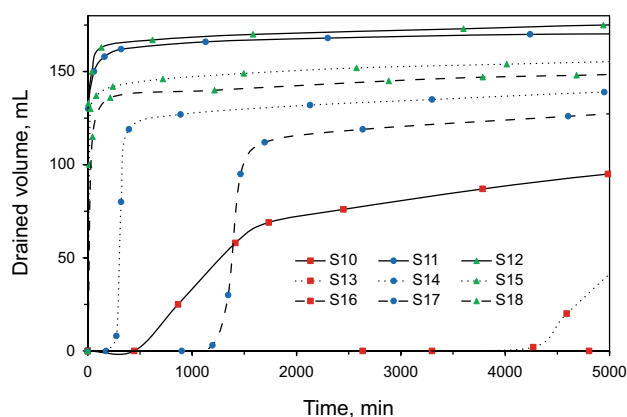**Fig. 3** Drained liquid volume for CGA-based fluid samples prepared with SDBS

Fig. 4 Drained liquid volume for CGA-based fluid samples prepared with CTAB

Table 2 Half-life time for CGA-based fluid samples prepared with SDBS

Fluid sample	S1	S2	S3	S4	S5	S6	S7	S8	S9
Base fluid volume in 250 mL dispersion, mL	100.0	97.2	96.2	115.2	112.2	110.8	132.6	128.7	126.8
Half-life time, min	1430	1455	1525	1820	1858	1885	2237	2280	2299

(a) CGA fluid sample S9   **(b)** CGA fluid sample S16
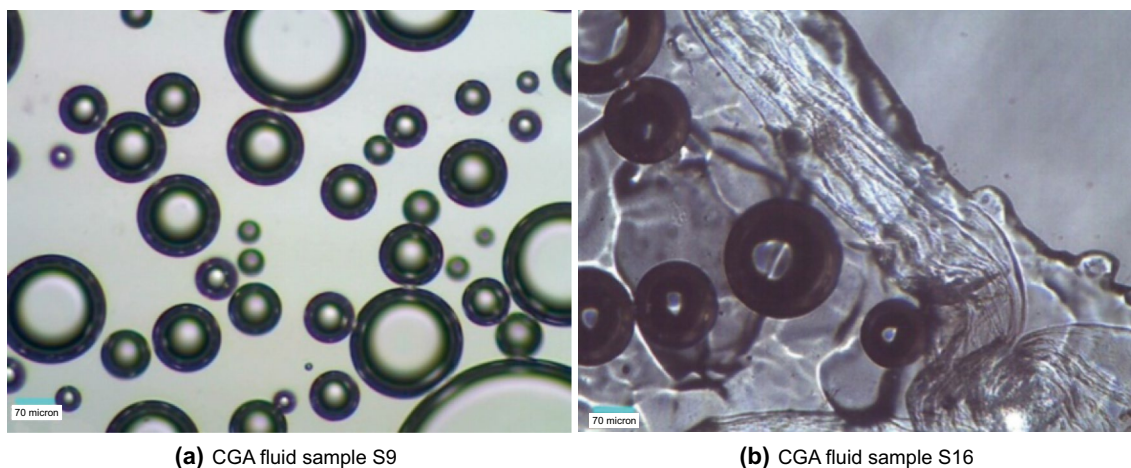
Fig. 5 Microscopic pictures of CGA fluid samples **a** S9 (6.86 g/L XG polymer and 0.80 g/L SDBS) and **b** S16 (6.86 g/L XG polymer and 0.35 g/L CTAB); white, long hair-like precipitates were observed in CGA fluid samples prepared with CTAB

the formation of these precipitates is due to physical properties of XG and CTAB, which are different in nature; XG is anionic in nature, while CTAB is cationic in nature which possibly accounts for the formation of precipitates. This could be the reason for the foam collapse at initial times. These precipitates could severely damage the formation near the wellbore and necessitate the costly stimulation to restore the initial permeability of the formation, the subject which is under study in continuation of this work.

It is guessed that for samples with surfactant concentrations higher than CMC, large amounts of surfactant molecules were available to react with the polymer and more precipitates were formed. Hence, the foam phase immediately broke down and the base fluid was rapidly drained from the dispersion. On the other hand, samples with minimum surfactant concentrations were stable for a long time so that sample S16 (with the highest polymer concentration and the lowest surfactant concentration) was stable during the test without any drained liquid. Generally, the more the difference between the polymer and surfactant concentrations for these samples, the more stable dispersions would be formed. Hence, samples S13 and S16 were stable for a considerable length of time while samples S11, S12, S15 and S18 were the least stable CGA fluids, which are in agreement with half-life time results (Table 3).

3.2 Rheology

The effect of polymer concentration on the shear stress and viscosity of CGA fluids at the SDBS concentration below CMC is shown in Fig. 6. As the polymer concentration increases, the base fluid viscosity also increases, which in turn raises the overall viscosity of the CGA fluid. At the surfactant concentration below CMC, an increase in polymer concentration results in an increase in the shear stress at lower shear rates and a decrease in shear stress at higher shear rates. This is preferable for CGA-based fluids because at low shear rates, viscosity should be high enough to prevent fluid invasion into the formation and suspend drilling cuttings whereas at high shear rates, it should be low enough to allow drilling fluids to be easily pumped into the well. Hence, the fluid samples with higher polymer concentration provide a wider range for viscosity data, and therefore, they are better candidates for CGA-based fluids. This is also true when the surfactant concentration is at CMC or above that (not presented here for the sake of brevity).

Table 3 Half-life time for CGA-based fluid samples prepared with CTAB

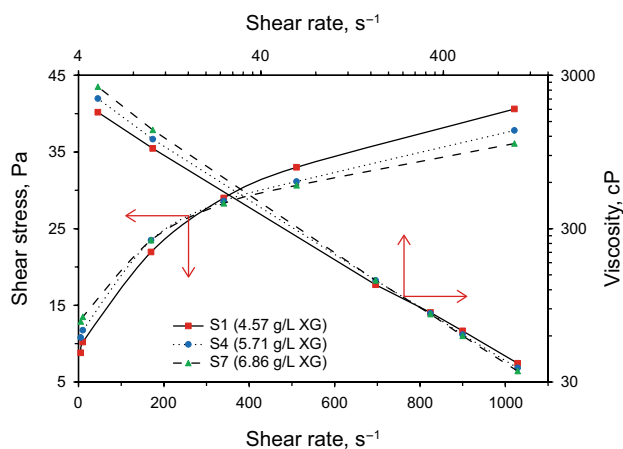| Fluid sample	S10	S11	S12	S13	S14	S15	S16	S17	S18
Base fluid volume in 250 mL dispersion, mL	160.6	182.3	205.9	157.7	162.8	200.0	155.5	157.7	188.2
Half-life time, min	2930	< 5	< 5	6040	323	15	Stable	1435	35

Fig. 6 Effect of XG concentration on shear stress and viscosity of CGA fluids at 0.34 g/L SDBS

The effect of SDBS concentration on shear stress and viscosity of CGA-based fluids at the polymer concentration of 6.86 g/L is shown in Fig. 7. When the surfactant concentration increases, more bubbles are produced which subsequently increase the viscosity of the CGA fluid. As can be seen from Fig. 7, the shear stress data points of sample fluid S9 with the highest surfactant concentration lie above those of other fluid samples. This leads to an increase in viscosity at low shear rates which is an important parameter for a good CGA-based drilling fluid. In fluid samples S7, S8, and S9, the shear stress at high shear rates increases with an increase in surfactant concentration. Among CGA fluid samples prepared with SDBS surfactant, it seems that samples S8 and S9 show better rheological behavior and provide a wider range for viscosity.

Among the CGA-based fluid samples prepared with CTAB surfactant, only CGA fluid samples S10, S13, and
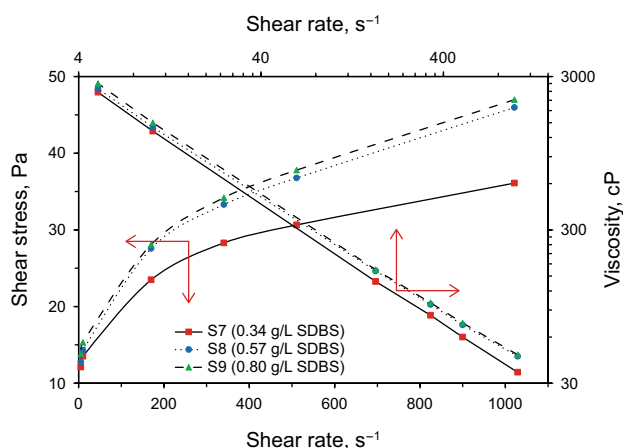

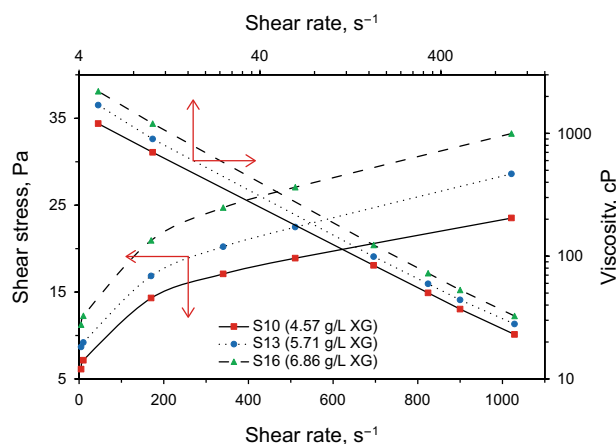**Fig. 7** Effect of SDBS concentration on shear stress and viscosity of CGA fluids at 6.86 g/L XG

S16 had good rheological properties. Figure 8 shows the effect of polymer concentration at CMC concentration of CTAB on the shear stress and viscosity of CGA-based fluids. Shear stress and viscosity data points related to fluid sample S16 with the highest polymer concentration lie above data of other fluid samples, and hence, this fluid sample shows better rheological behavior.

Fig. 8 Effect of XG concentration on shear stress and viscosity of CGA fluids at 0.35 g/L CTAB

3.3 Image analysis

The size of bubbles should be proportionate to the pore and throat size distribution of the formation rock. Thus, for an effective sealing of the formation pores during drilling operations, the size and size distribution of bubbles should be determined before implementation in the field. Figure 9 shows the typical microscopic pictures of CGA fluid samples S9 and S16 and their bubble size distribution immediately right after CGA fluid preparation.

At the SDBS concentration below CMC (at 0.34 g/L SDBS), the effect of XG polymer concentration on d_{50} and d_{90} of bubbles is shown in Fig. 10. At $t = 0$ (freshly prepared CGAs), the size of bubbles decreases with increasing polymer concentration. An increase in the polymer concentration makes difficult the introduction of air into the system and hence smaller bubbles are formed. The growth rate of aphrons with time is also shown in Fig. 10. As can be seen, d_{50} and d_{90} of CGAs increase because of the coarsening of aphrons and the disappearance of the smaller bubbles (Feng et al. 2009). Samples with higher concentrations of XG polymer exhibit less change in the size of bubbles with pass of time. Thus, through increasing the viscosity of the base fluid by addition of XG polymer, the stability of the CGA bubbles increases. This is also true when the SDBS concentration is at CMC value or above that (not presented here for the sake of brevity).

At the XG polymer concentration of 6.86 g/L, the effect of SDBS concentration on d_{50} and d_{90} of bubbles is shown in Fig. 11. For freshly prepared CGAs, the aphrons bubble size increases with increasing SDBS concentration. This trend contradicts the data presented by Chapalkar et al. (1993) who stated that an increase in the surfactant concentration should decrease the bubble diameter. Bjorndalen and Kuru (2008b) and Arabloo and Pordel (2014) found the same
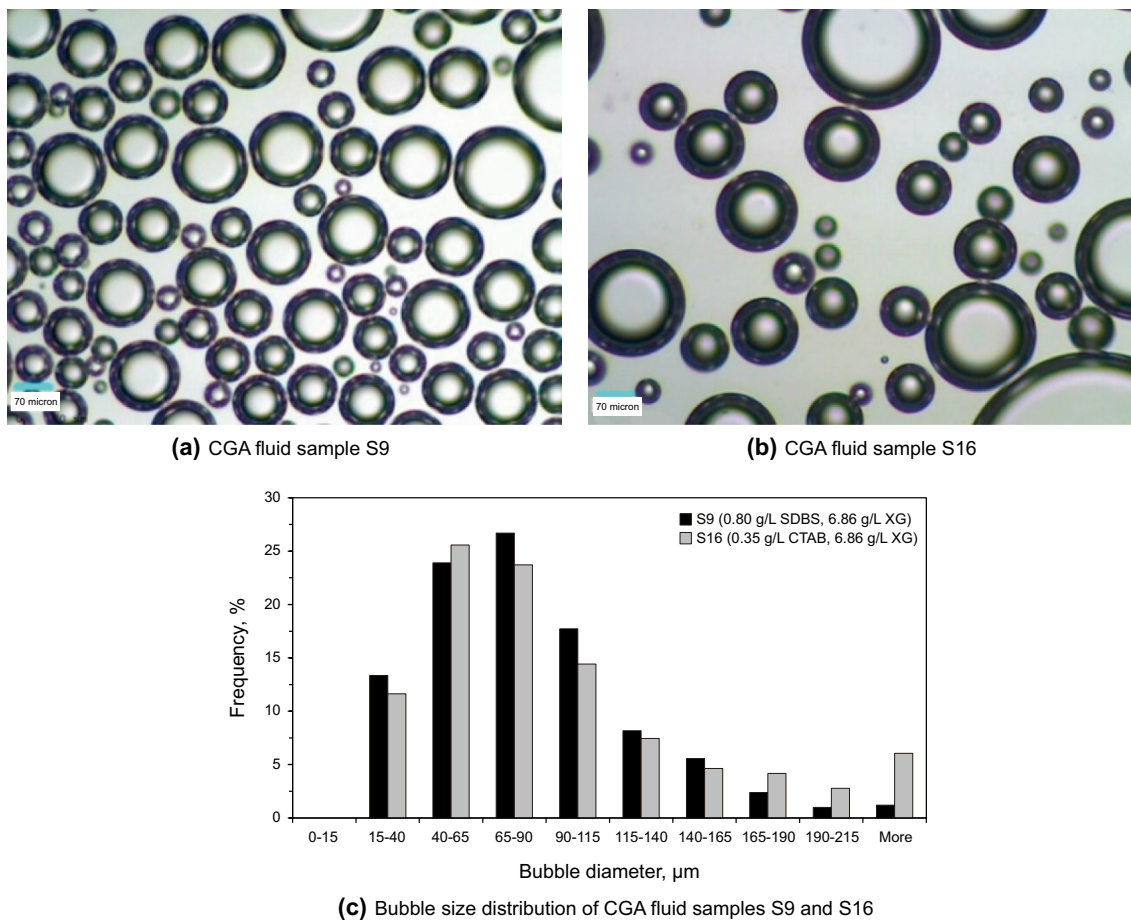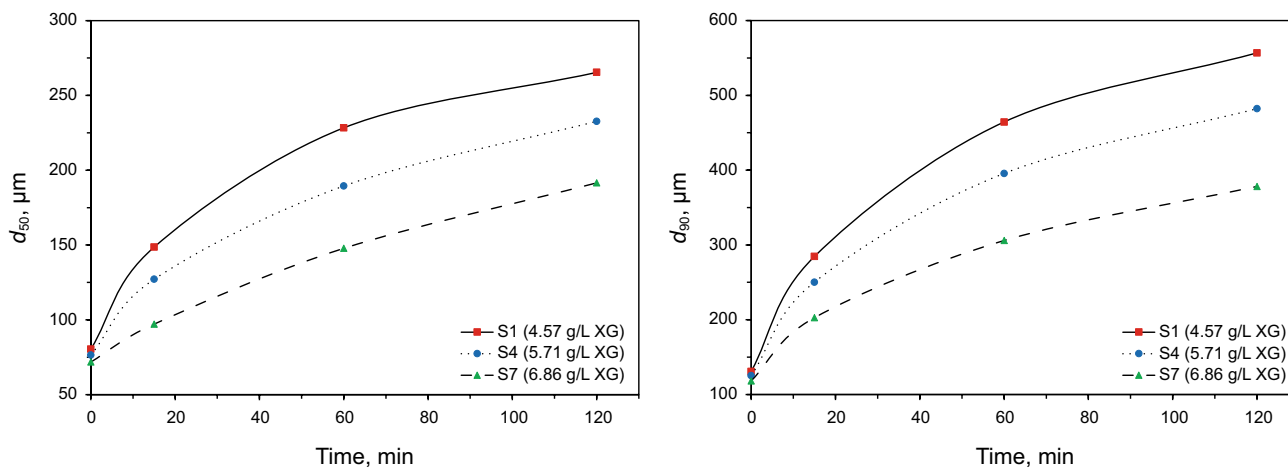

(a) CGA fluid sample S9

(b) CGA fluid sample S16

(c) Bubble size distribution of CGA fluid samples S9 and S16

Fig. 9 Microscopic pictures of CGA fluid samples **a** S9 and **b** S16 and **c** their bubble size distribution immediately right after fluid preparation

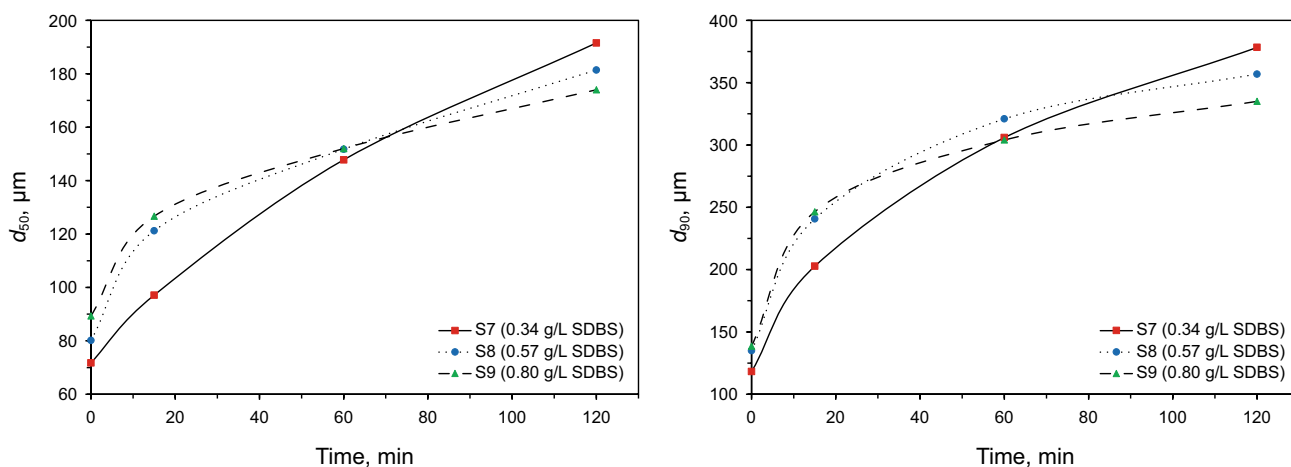**Fig. 10** Effect of XG polymer concentration on d_{50} and d_{90} of CGA-based fluids at 0.34 g/L SDBS

Fig. 11 Effect of SDBS concentration on d_{50} and d_{90} of CGA-based fluids at 6.86 g/L XG
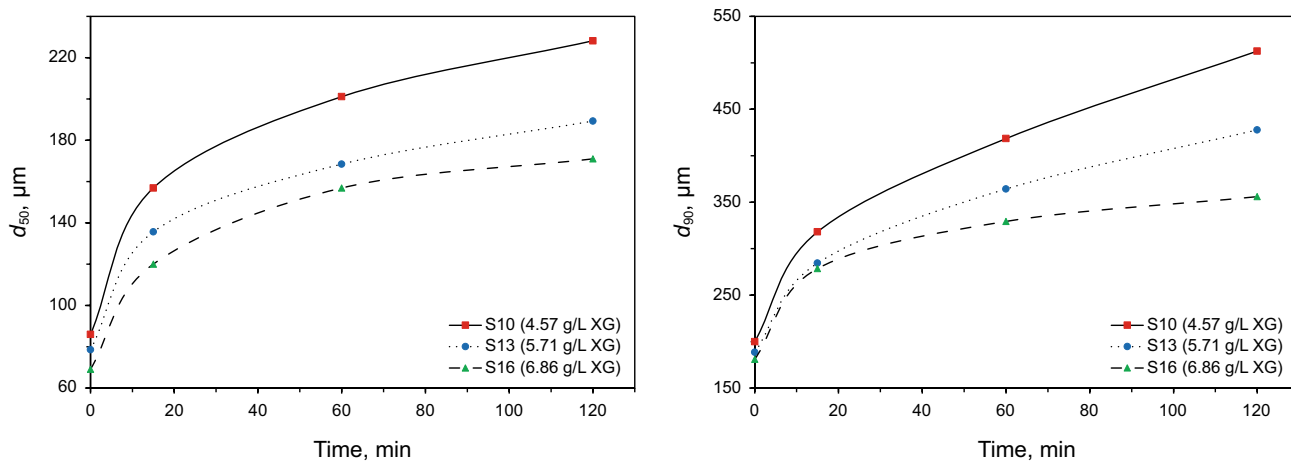

Fig. 12 Effect of XG polymer concentration on d_{50} and d_{90} of CGA-based fluids at 0.35 g/L CTAB

results. This contradiction might be due to alteration of the aphronization process by changing the base fluid from deionized water to XG-water solution in this study. The effect of surfactant concentration on the growth rate of aphron bubbles is also investigated (Fig. 11). Experimental results show that in samples with higher surfactant concentration, CGAs have been less affected by the pass of time and are more stable. This could be due to the fact that with an increase in the concentration of surfactant, more surfactant molecules are available at the bubble surface and stabilize CGAs.

Among CGA fluid samples prepared with CTAB, only fluid samples S10, S13, and S16 had good stability and rheological properties. In other fluid samples prepared with CTAB, the formation of large amounts of white, long hair-like precipitates causes the foam phase to break down rapidly. Figure 12 shows the effect of polymer concentration on d_{50} and d_{90} of bubbles at the CTAB concentration of 0.35 g/L. As in the case for SDBS, the size of the bubbles decreases with increasing polymer concentration. Also, samples S13 and S16 with higher concentrations of XG polymer exhibit less change in the size of bubbles with the pass of time. Fluid sample S16 is preferred for CGA-based fluids due to its better stability and rheological properties compared to other fluid samples prepared with CTAB.

4 Conclusions

In this study, a comprehensive experimental study was conducted to choose the appropriate formulation for CGA-based fluids. The effects of polymer and surfactant concentrations and surfactant type on the physicochemical characteristics of CGA-based fluids were studied. Static stability tests, rheological behavior, and bubble size analyses of CGAs were performed. The following are the main conclusions of this study:

1. For CGA fluid samples prepared with SDBS, an increase in the polymer and surfactant concentrations improved the stability of CGA fluids. The polymer concentration greatly influenced the stability of CGA fluids while the surfactant concentration did not strongly affect it. However, CGA-based fluids prepared with CTAB exhibited different behavior, the formation of white, long hair-like precipitates was the main reason for their unusual behavior. The more the difference between the polymer and surfactant concentrations, the more stable dispersion was formed.
2. An increase in the XG polymer concentration resulted in an increase in the shear stress at lower shear rates and a decrease in the shear stress at higher shear rates.
3. The bubble size of CGAs was significantly influenced by the polymer and surfactant concentrations. The most stable CGAs were formed at higher concentrations of polymer.
4. Regarding results of the experiments conducted in this study, fluid samples S9 and S16 prepared with SDBS and CTAB surfactants, respectively, are the best choices for CGA-based fluids.

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